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Research Article

Raman Spectroscopy of Amorphous Carbon Prepared by Pulsed Arc Discharge in Various Gas Mixtures

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To meet various application requirements, it is important to enable an improvement of a-C structure and properties, such as hardness, adhesion, and wear resistance. In this study, we used the Raman spectroscopy to investigate the a-C thin films structure dependence on the different deposition parameters. The effect of nitrogen, argon, and hydrogen gas flow rate was analyzed to determine the influence on the film properties. The change in the gas type, combination, and flow had a significant influence on the D and G bands of the a-C Raman spectra. The addition of N_2 into the chamber promoted the sp^2 creation, while with adding hydrogen the layer contained more sp^3 bonds. The depositions of a-C thin films were carried out in pulsed arc discharge vacuum installation. Micro-Raman measurements of the deposited materials were performed using an ISA Dilor-Jobin Yvon-Spex Labram confocal system with 632.8 nm radiation from a He-Ne laser using a back-scattering geometry.

1. Introduction

In recent years, a lot of work has been focused on the synthesis of novel carbon thin films materials, especially crystalline diamond, amorphous carbon (a-C), and carbon nitride (a-C:N) which offers excellent tribological, optical, electrical, and other properties with the additional advantage that carbon is a biocompatible material. The huge range of properties achievable in carbon coatings is mainly due to the ability of carbon to form different types of interatomic bonds, to take up different sites, and to adopt different structures. However, for each application, there are different requirements on the film properties, for example, the adhesion level achievable and coating cost. Therefore, several methods to influence the a-C films structure, composition, and thus the properties, such as variation of ion energy, plasma treatment, pressure, and the use of different gases were presented [1–6].

Raman spectroscopy can be applied as a simple and accurate identification method of different carbon phases within the film. Due to its sensitivity to variation of translation symmetry, Raman spectroscopy allows distinguishing several types of carbon such as diamond, graphite, diamond-like carbon, and carbon nitride. The Raman spectra of nanocrystalline and amorphous carbon are dominated by the D (D for disorder) and G (G for graphite) peaks with varied intensity, position, and band width [7–11]. The G band at approximately 1540–1600 cm^{-1} corresponds to the symmetric E_{2g} mode in graphite-like materials, while the D band at 1350 cm^{-1} arises from the limitations in the graphite domain size, induced by grain boundaries or imperfections, such as substitutional N atoms, sp^3 carbon, or impurities. The D peak is not present in perfect single crystal graphite and becomes active only in the presence of disorder. For visible excitation, the G and D peaks are due to sp^2 sites only. The sp^2 sites have such a high cross-section that they dominate the spectra, the sp^3 sites are invisible, and the spectrum responds only to the configuration or order of the sp^2 sites. The Raman

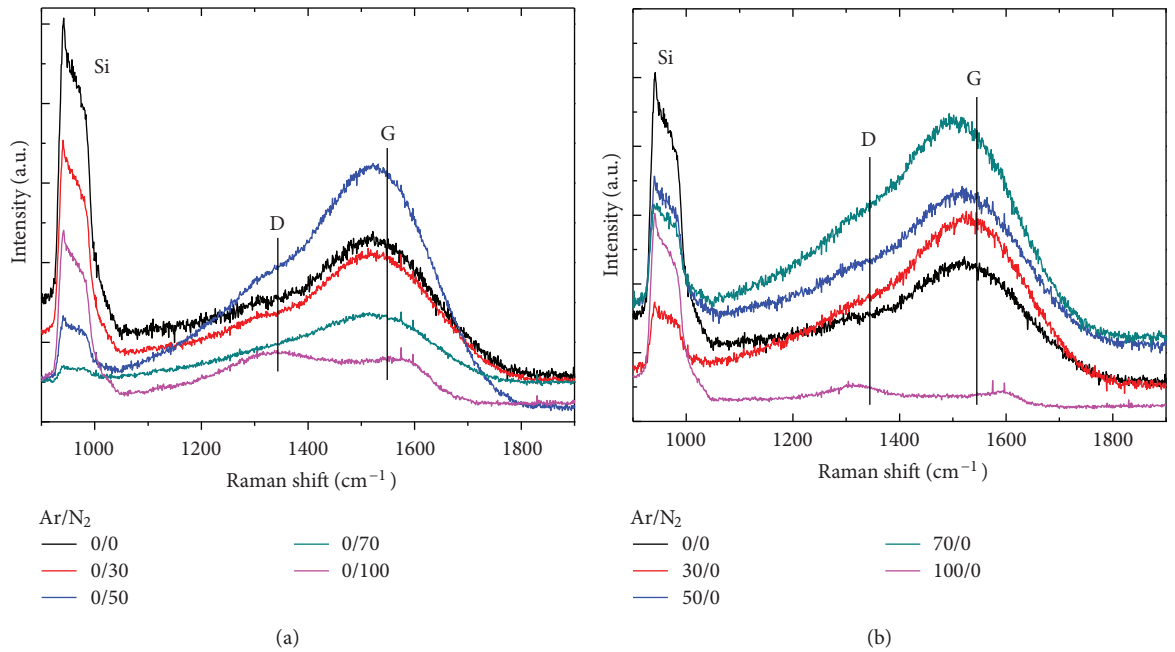

FIGURE 1: Raman spectra of a-C(:N) films deposited with various N_2 (a) and Ar (b) flows.

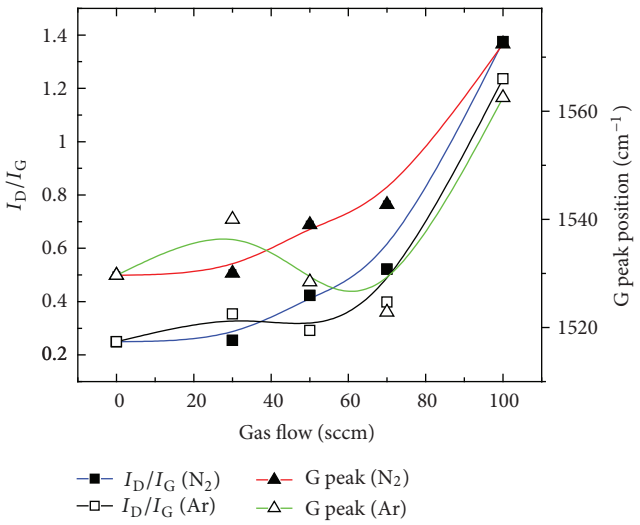

FIGURE 2: I_D/I_G and G peak position dependence of the films deposited with various N_2 and Ar flows.

spectra of a-C depend on (1) clustering of the sp^2 phase; (2) bond length and bond angle disorder; (3) presence of sp^2 rings or chains; (4) the sp^2/sp^3 ratio. The spectra directly depend on the quality or configuration of the sp^2 phase and only indirectly on the quantity of the sp^2 phase. Most times the sp^2 configuration varies consistently with the sp^2 fraction. However, in some cases, the sp^2 quality can be changed independently from the sp^2/sp^3 ratio [12–17]. A weak peak at 2200 cm^{-1} is attributed to triple C–N bonds and appears in the case of high nitrogen doping. The second-order silicon peak which appeared at 960 cm^{-1} can be used to measure the transparency of the film. The I_{Si}/I_G ratio increases with the increase of N content in the film, revealing a reduction in the optical band gap when more N atoms are incorporated in films [18]. In this study, we used the Raman spectroscopy to investigate a-C thin films structure and its dependence on the gas type and flow.

2. Experimental

The depositions of amorphous carbon thin films were carried out in a vacuum installation type UVNIPA-1-001 described previously [19]. The sputtering frequency of the arc source pulses was 5 Hz. Background pressure was 10^{-4} Pa and working pressure was maintained around 1 Pa according to gas flow. Argon and nitrogen gas flow was varied from 0 to 100 sccm and the flow of hydrogen from 20 to 60 sccm. The deposition temperature was kept below 100°C. Mirror polished silicon substrates were used for deposition of the coatings. Before deposition of the layer, substrates were cleaned for 10 min with Ar ions within one vacuum cycle. The effects of nitrogen, argon, and hydrogen gas flow on the film properties were investigated by Raman spectroscopy. Micro-Raman measurements of the deposited materials were performed using an ISA Dilor-Jobin Yvon-Spex Labram confocal system with 632.8 nm radiation from a He-Ne laser using a back-scattering geometry. Microscope objective ×80 was used to focus the laser beam onto a spot of approximately 1–5 μm in diameter and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. The acquired Raman spectra were fitted with a Gaussian line to illustrate the G peak position and I_D/I_G ratio. The XPS investigations were performed in an Omicron UHV system

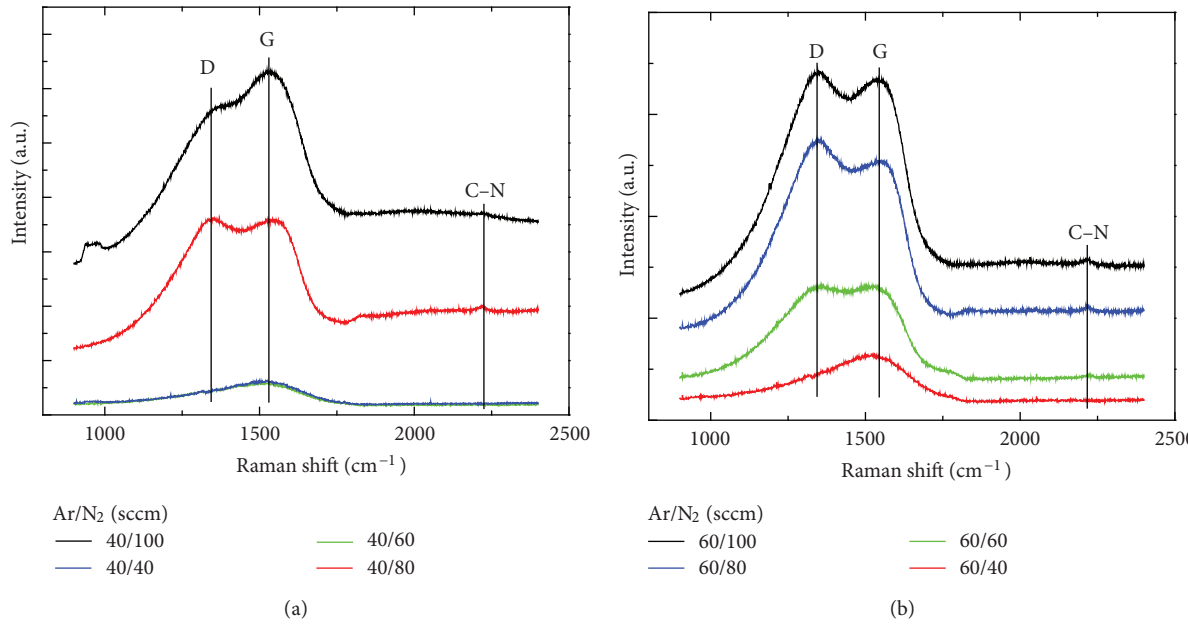

Figure 3: Raman spectra of a-C:N films deposited with constant Ar flow and various N_2 flows.

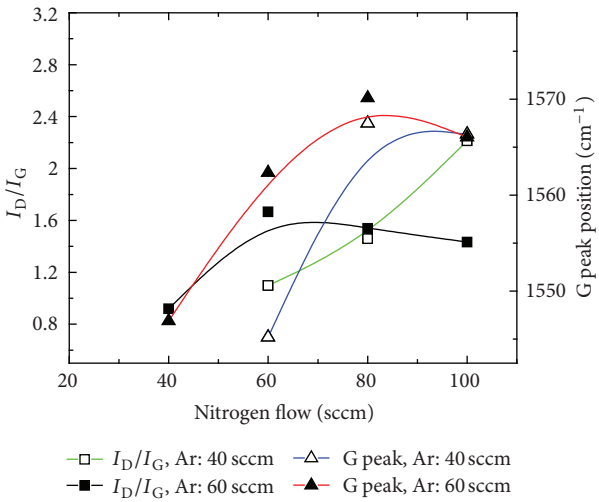

Figure 4: I_D/I_G and G peak position dependence of the films deposited with constant Ar flow and various N_2 flows.

equipped with an EA 125 hemispherical electron analyzer using monochromated AlK radiation (excitation energy h = 1486.7 eV). The samples have been annealed by radiative heating from the backside at 500°C for 10 min in UHV conditions. The calibration of the energy scale was made by comparison to reference measurements on a polycrystalline silver sample and HOPG.

3. Results and Discussion

Raman spectra of the films deposited with various argon or nitrogen flow during the deposition process are shown in Figure 1. We can see that, with changing both Ar and N_2 flow the intensity maximum of all three depicted bands (Si, D, G band) changes significantly. The maximum intensity in Si band falls with increasing the process gas flow from 0 to 100 sccm. This indicates lowered transparency of the films due to the growth of a thicker layer and also due to more graphitic character of the films deposited with higher Ar or N_2 flow [18]. Figure 2 shows the I_D/I_G ratio and G peak position dependence of the films from Figure 1. For the layers deposited in nitrogen atmosphere both I_D/I_G and G peak position increases as the amount of N_2 in the chamber during deposition rises. The I_D/I_G ratio is 0.25 for pure a-C film and 1.35 for film deposited with 100 sccm of N_2 flow. The G peak position rises from 1518 cm^{-1} for a-C to 1574 cm^{-1} for a-C:N with 100 sccm of nitrogen flow. The simultaneous growth of both I_D/I_G ratio and G peak position with increasing of nitrogen flow is a reliable indicator of sp^3/sp^2 ratio decrease and corresponds to another research [20]. From the spectra, we can assume that, nitrogen creates rather sp^2 than sp^3 bonds and the films become more graphitic when the N_2 flow rises, which is similar to other studies [11, 14, 18].

The I_D/I_G ratio and G peak position of the films deposited with various Ar flow shows slight grow from 0 to 30 sccm, drop around 60 sccm and sharp increase for films deposited in atmosphere with 100 sccm of Ar flow. The films around 60 sccm Ar flow have the lowest I_D/I_G ratio and it seems such a moderate Ar flow is optimal for deposition of the films with higher sp^3/sp^2 ratio. Further increasing of Ar flow caused more graphitic bonds within the films.

Raman spectra of the a-C:N films deposited with combined Ar/N_2 flow are shown in Figure 3. The Ar flow was set constant to the values with best results from previous depositions (40 and 60 sccm) while the N_2 flow was changed from 40 to 100 sccm to estimate the influence of nitrogen in the combined gas flow. From I_D/I_G ratio and G peak

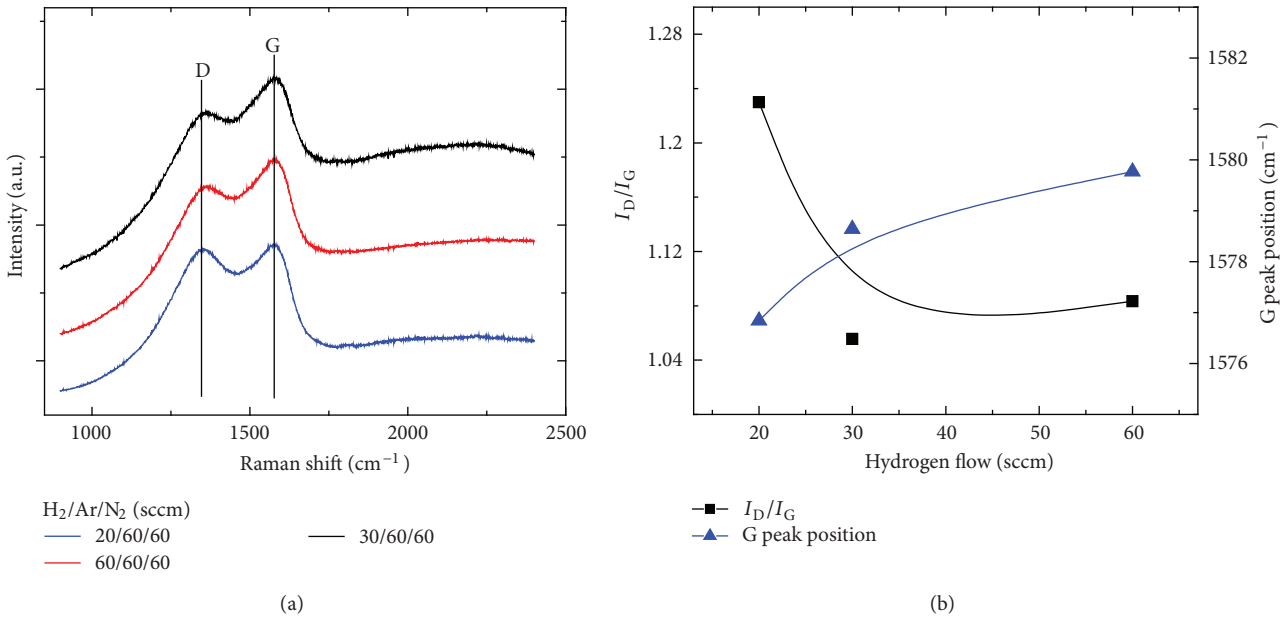

FIGURE 5: Raman spectra of a-C:N:H grown with constant Ar/N$_2$ flow (a), I_D/I_G and G peak position dependence of the films (b).

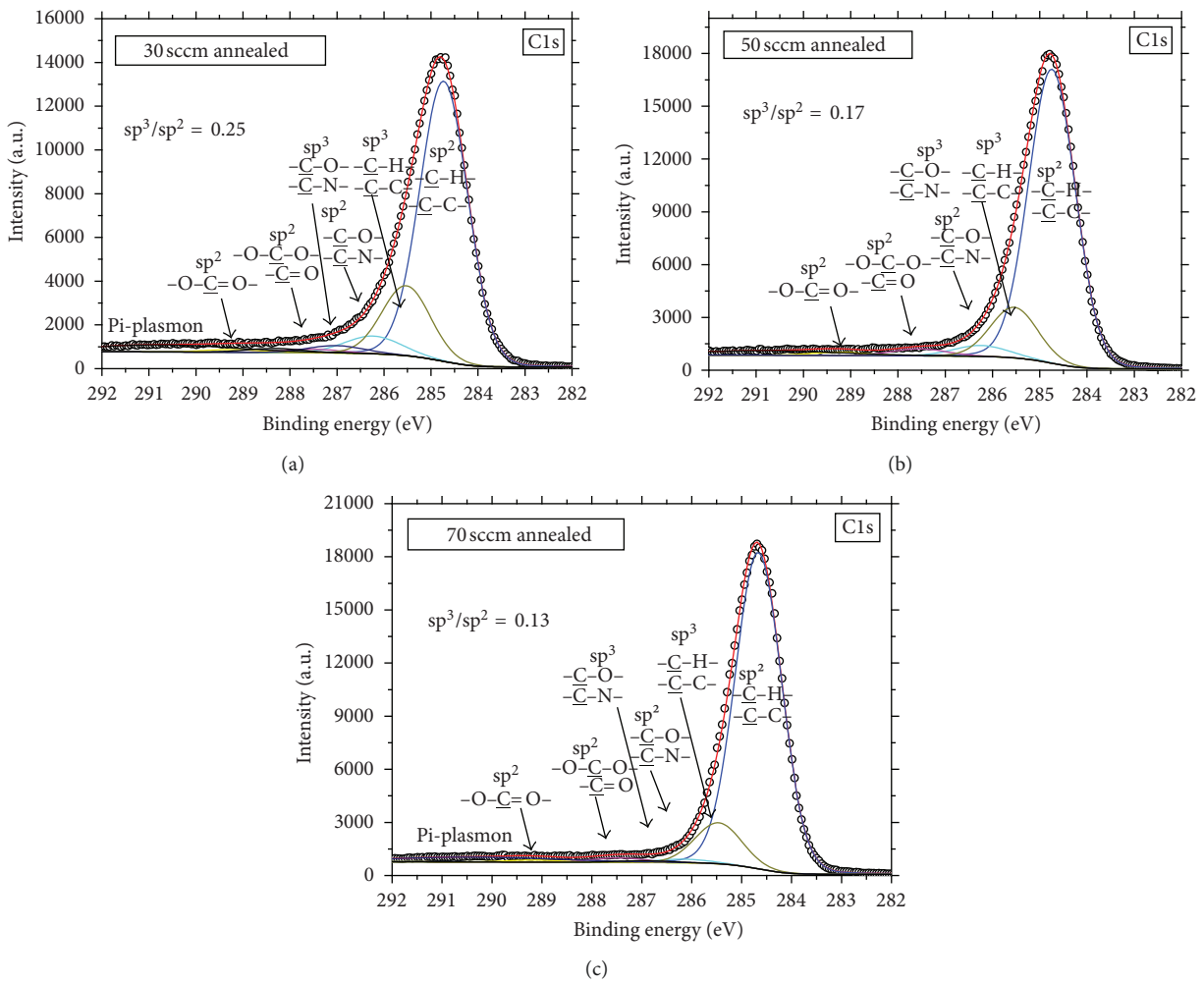

FIGURE 6: The XPS spectra of the a-C:N films deposited with 30, 50, and 70 sccm of N$_2$.

position dependence shown in the Figure 4 it is obvious that, for the films deposited with 40 and 60 sccm argon flows, the maximum of G peak position is around 80 and 60 sccm of nitrogen flow, respectively. The values of I_D/I_G ratio and G peak position for all gas combined depositions are higher than for layers deposited with only one gas type. Therefore, we can assume that, the further Ar/N_2 admixture into the chamber during deposition process promotes the creation of sp^2 bonding in the thin film. Besides the main D and G broad peaks, with increasing the N_2 flow we can observe also a small local maximum at approximately 2200 cm^{-1} attributed to triple C–N bonds. This band is characteristic with very small intensity in the Raman spectra made using visible laser excitation [21, 22].

Figure 5 shows the Raman spectra and data abstracted from fitting of the films deposited with constant Ar/N_2 flow while adding H_2 into the gas mixture. As we can see, the I_D/I_G ratio decreased from 1.6 for nonhydrogenated a-C:N to 1.1 due to the presence of hydrogen in the gas mixture. The G peak position is changing only slightly towards higher values. The creation of sp^2 phase is due to the hydrogen addition lower. This may be due to hydrogen affecting as an etchant of graphitic bonds during growth of the film causing the higher sp^3 content.

For comparison, XPS analysis of the a-C:N samples deposited with 30, 50, and 70 sccm of N_2 flow was made (Figure 6). The resulting sp^3/sp^2 ratio decreased with nitrogen flow increasing. The results correspond to the Raman measurements made on these samples and are in agreement with other studies [13, 15, 18].

4. Conclusions

We deposited continuous, homogeneous, and adhesive a-C, a-C:N and a-C:N:H thin films on Si substrates using pulsed vacuum arc discharge technique. Following the Raman spectra we found that, with adding different gases with various concentrations the film structure and properties change significantly. The addition of N_2 and/or Ar caused the simultaneous growth of both I_D/I_G ratio and G peak position which is a reliable indicator of sp^3/sp^2 ratio decrease and increase of graphitic contents in the films. The films with only a moderate Ar flow had lower I_D/I_G ratio and this was found to be optimal for deposition of the films with high sp^3/sp^2 ratio. The addition of hydrogen into the gas mixture caused the decrease in I_D/I_G ratio and thus we can expect lower amount of graphitic sp^2 bonding. We found that, the maximum intensity of Si band falls with increasing of the process gas flow. This indicates lowered transparency of the films due to the growth of a thicker layer and also due to the more graphitic character of films deposited with higher Ar and/or N_2 flow.

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References

[1] J. Robertson, "Diamond-like amorphous carbon," *Materials Science and Engineering R*, vol. 37, no. 4–6, pp. 129–281, 2002.

[2] W. Ensinger, "Correlations between process parameters and film properties of diamond-like carbon films formed by hydrocarbon plasma immersion ion implantation," *Surface and Coatings Technology*, vol. 203, no. 17-18, pp. 2721–2726, 2009.

[3] S. Neuville and A. Matthews, "A perspective on the optimisation of hard carbon and related coatings for engineering applications," *Thin Solid Films*, vol. 515, no. 17, pp. 6619–6653, 2007.

[4] G. A. Viana, E. F. Motta, M. E. H. M. da Costa, F. L. Freire Jr., and F. C. Marques, "Diamond-like carbon deposited by plasma technique as a function of methane flow rate," *Diamond and Related Materials*, vol. 19, no. 7–9, pp. 756–759, 2010.

[5] H. Ma, L. Zhang, N. Yao, B. Zhang, H. Hu, and G. Wen, "The effect of nitrogen addition on field emission of diamond-like carbon films," *Diamond and Related Materials*, vol. 9, no. 9-10, pp. 1608–1611, 2000.

[6] S. Da-Cheng, L. Yi-Chun, L. Yan, Q. Xiu-Ying, and Z. Dian-Qiang, "Structural and electrical properties of amorphous hydrogen carbon-nitrogen films," *Chinese Physics Letters*, vol. 21, no. 2, article 400, 2004.

[7] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, pp. 14095–14107, 2000.

[8] A. C. Ferrari, "Determination of bonding in diamond-like carbon by Raman spectroscopy," *Diamond and Related Materials*, vol. 11, no. 3–6, pp. 1053–1061, 2002.

[9] J. Filik, P. W. May, S. R. J. Pearce, R. K. Wild, and K. R. Hallam, "XPS and laser Raman analysis of hydrogenated amorphous carbon films," *Diamond and Related Materials*, vol. 12, no. 3–7, pp. 974–978, 2003.

[10] J. R. Shi, Y. J. Xu, and J. Zhang, "Study on amorphous carbon nitride film prepared by facing target sputtering," *Thin Solid Films*, vol. 483, no. 1-2, pp. 169–174, 2005.

[11] L. Valentini, J. M. Kenny, Y. Gerbig et al., "Structure and mechanical properties of argon assisted carbon nitride films," *Thin Solid Films*, vol. 398-399, pp. 124–129, 2001.

[12] J. Li, W. T. Zheng, Z. Jin et al., "Influence of substrate dc bias on chemical bonding, adhesion and roughness of carbon nitride films," *Applied Surface Science*, vol. 191, no. 1–4, pp. 273–279, 2002.

[13] J. R. Shi, X. Shi, Z. Sun, S. P. Lau, B. K. Tay, and H. S. Tan, "Resonant Raman studies of tetrahedral amorphous carbon films," *Diamond and Related Materials*, vol. 10, no. 1, pp. 76–81, 2001.

[14] V. Kopustinskas, S. Meskinis, V. Grigaliunas et al., "Ion beam synthesis of α-CN_x:H films," *Surface and Coatings Technology*, vol. 151-152, pp. 180–183, 2002.

[15] R. Hauert, A. Glisenti, S. Metin et al., "Influence of nitrogen doping on different properties of a-C:H," *Thin Solid Films*, vol. 268, no. 1-2, pp. 22–29, 1995.

[16] S. C. H. Kwok, P. Yang, J. Wang, X. Liu, and P. K. Chu, "Hemocompatibility of nitrogen-doped, hydrogen-free diamond-like carbon prepared by nitrogen plasma immersion

ion implantation-deposition," *Journal of Biomedical Materials Research A*, vol. 70, no. 1, pp. 107–114, 2004.

[17] L. Y. Chen, C.-Y. Cheng, and F. C. Hong, "Properties of carbon nitride (CN_x) films deposited by a high-density plasma ion plating method," *Diamond and Related Materials*, vol. 11, pp. 1172–1177, 2002.

[18] S. S. Roy, S. S. Roy, R. McCann, P. Papakonstantinou, P. Maguire, and J. A. McLaughlin, "The structure of amorphous carbon nitride films using a combined study of NEXAFS, XPS and Raman spectroscopies," *Thin Solid Films*, vol. 482, no. 1-2, pp. 145–150, 2005.

[19] M. Marton, E. Zdraveckáb, M. Vojs et al., "Study of adhesion of carbon nitride thin films on medical alloy substrates," *Vacuum*, vol. 84, no. 1, pp. 65–67, 2010.

[20] J. H. Sui, Z. Y. Gao, W. Cai, and Z. G. Zhang, "DLC films fabricated by plasma immersion ion implantation and deposition on the NiTi alloys for improving their corrosion resistance and biocompatibility," *Materials Science and Engineering A*, vol. 454-455, pp. 472–476, 2007.

[21] N. A. Morrison, S. E. Rodil, J. Robertson, and W. I. Milne, "Chemical sputtering of ta-C: implications for the deposition of carbon nitride," *Journal of Applied Physics*, vol. 89, no. 10, pp. 5754–5759, 2001.

[22] A. C. Ferrari, S. E. Rodil, and J. Robertson, "Resonant Raman spectra of amorphous carbon nitrides: the G peak dispersion," *Diamond and Related Materials*, vol. 12, no. 3–7, pp. 905–910, 2003.